

First Principles Phase Diagram Calculations for the Octahedral-Interstitial System HfO_X , $0 \leq X \leq 1/2$

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Abstract

First principles based phase diagram calculations were performed for the hexagonal closest packed octahedral-interstitial solid solution system αHfO_X ($\alpha Hf[]_{1-X}O_X$; $[]$ =Vacancy; $0 \leq X \leq 1/2$). The cluster expansion method was used to do a ground state analysis, and to calculate the phase diagram. The predicted diagram has four ordered ground-states in the range $0 \leq X \leq 1/2$, but one of these, at $X=5/12$, is predicted to disproportionate at $T \approx 220K$. At $X \approx 1/3$ (Hf_3O) and $X \approx 1/2$ (Hf_2O), order-parameter vs temperature plots evince a cascade of ordered structures.

Key words: HfO_X ; Hf suboxides; Devil's Staircase; Long-Period Superstructures; First Principles Phase diagram calculation.

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The group 4 hexagonal closest packed (hcp) suboxides MO_X ($M = Ti, Zr$ or Hf) all exhibit octahedral interstitial ordering of oxygen, O , and vacancies, $[]$, in solid solutions of the form $\alpha M[]_{1-X}O_X$, $0 \leq X \leq 1/2$). By far, the most studied of these systems is ZrO_X , because of issues related to the oxidation of Zircalloy cladding on UO_2 fuel rods in light-water reactors.^{1–16} The hcp-based HfO_X system has attracted less attention,^{17–20} but Hafnium alloys are also potential cladding materials; e.g. for long-lived nuclear waste transmutation applications in Boiling Water Reactors.²¹ Also, investigating the chemical systematics of all three group 4 suboxides enhances understanding of each binary system. In the ZrO_X system, long-period superstructure (LPSS) phases were reported^{4,5} in samples with $X \approx 1/3$, but not predicted in a recent first principles phase diagram (FPPD) calculation¹⁶; however, in the HfO_X FPPD calculations described below, a cascade of related ordered structures is predicted at $X \approx 1/3$ and $X \approx 1/2$; it is not yet clear if this cascade constitutes a Devil’s Staircase.^{22,23}

I. METHODOLOGY

A. Total Energy Calculations

Formation energies, ΔE_f (Fig. 1) were calculated for fully relaxed hcp αHf , HfO (hcp αHf with all octahedral interstices occupied by O), and 96 $\alpha Hf[]_{1-n}O_n$ supercells of intermediate composition. All calculations were performed with the density functional theory (DFT) based Vienna *ab initio* simulation program (VASP, version 4.4.5^{24,25}) using projector-augmented plane-wave pseudopotentials, and the generalized gradient approximation for exchange and correlation energies. Electronic degrees of freedom were optimized with a conjugate gradient algorithm, and both cell constant and ionic positions were fully relaxed.

Total energy calculations were converged with respect to k-point meshes by increasing the density of k-points for each structure until convergence is achieved. A 500 eV energy cutoff was used, in the “high precision” option which guarantees that *absolute* energies are converged to within a few meV/site (a few tenths of a kJ/site of exchangeable species; O , $[]$). Residual forces were typically 0.02 eV or less.

Calculated formation energies, ΔE_f , relative to a mechanical mixture of $\alpha Hf + \alpha HfO$,

for the $106 \alpha Hf[]_{1-n}O_n$ supercells are plotted as solid circles in Fig. 1. Values of ΔE_f are,

$$\Delta E_f = (E_{Str} - E_{\alpha Hf} - E_{\alpha HfO})/(2) \quad (1)$$

where: E_{Str} is the total energy of the $\alpha Hf[]_{1-n}O_n$ supercell; $E_{\alpha Hf}$ is the energy/atom of αHf ; $E_{\alpha HfO}$ is the energy/atom of αHfO .

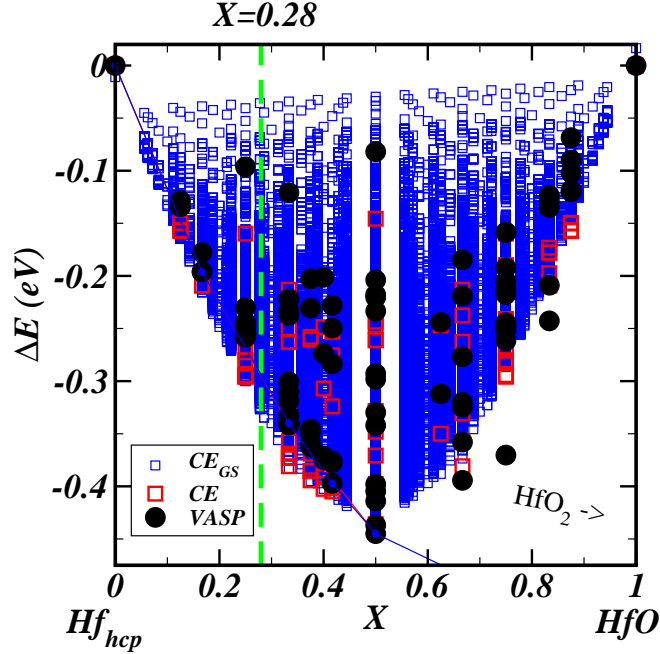


FIG. 1: Comparison of VASP (large solid circles) and CE (larger open squares, red online) formation energies, ΔE_f , and a ground-state analysis on structures with 18 or fewer octahedral-interstitial sites (smaller open squares, blue online). Extension of the convex hull towards the formation energy of monoclinic Hafnia, HfO_2 , indicates that the four ordered GS at $X=1/6, 1/3, 5/12$ and $1/2$ are predicted to be GS of the $Hf - O$ binary. This is not in agreement with experiment which suggests that the solubility limit is approximately $HfO_{0.28}$ ($X_{max} \approx 0.28$; vertical dashed line, green online); i.e. in the solid solution $Hf_{1-Y}O_Y$, $Y \approx 0.22$.

B. The Cluster Expansion Hamiltonian

The cluster expansion, CE²⁶, is a compact representation of the configurational total energy. In the $\alpha\text{Hf}[]_{1-X}\text{O}_X$ system, the solid solution configuration is described by pseudospin occupation variables σ_i , which take values $\sigma_i = -1$ when site- i is occupied by $[]$ and $\sigma_i = +1$ when site- i is occupied by O .

The CE parameterizes the configurational energy, per exchangeable cation, as a polynomial in pseudospin occupation variables:

$$E(\sigma) = \sum_{\ell} m_{\ell} J_{\ell} \left\langle \prod_{i \in \ell'} \sigma_i \right\rangle \quad (2)$$

Cluster ℓ is defined as a set of lattice sites. The sum is taken over all clusters ℓ that are not symmetrically equivalent in the high-T structure space group, and the average is taken over all clusters ℓ' that are symmetrically equivalent to ℓ . Coefficients J_{ℓ} are called effective cluster interactions, ECI, and the *multiplicity* of a cluster, m_{ℓ} , is the number of symmetrically equivalent clusters, divided by the number of cation sites. The ECI are obtained by fitting a set of VASP FP calculated structure energies, $\{E_{Str}\}$. The resulting CE can be improved as necessary by increasing the number of clusters ℓ and/or the number of E_{Str} used in the fit.

Fitting was performed with the Alloy Theoretic Automated Toolkit (ATAT)^{25,27–29} which automates most of the tasks associated with the construction of a CE Hamiltonian. A complete description of the algorithms underlying the code can be found in²⁸. The zero- and point-cluster values were -0.571537 eV and 0.013973 eV, respectively. The six pair and one 3-body ECI are plotted in Figs. 2a and 2b (open symbols, red online), as are ECI for ZrO_X (solid black symbols) and TiO_X (open symbols, blue online). As in ZrO_X and TiO_X , nearest neighbor (nn) $\text{O}-\text{O}$ pairs are highly energetic, and therefore strongly avoided; hence nn-pair ECI are strongly *attractive* (ECI >0, for $\text{O}-[]$ nn pairs); but beyond nn-pairs, the pairwise ECI are smaller; however the 3rd and 4th nn pair-ECI in HfO_X are significantly larger than corresponding terms for ZrO_X and TiO_X . As in ZrO_X , the ratio of ECI parallel (J_{\parallel}) and perpendicular (J_{\perp}) to c_{Hex} , respectively, is $J_{\parallel}/J_{\perp} \approx 2.5$; for TiO_X , $J_{\parallel}/J_{\perp} \approx 5$. These results are similar to those presented by Ruban et al.³⁰, although the ECI presented here are not identically comparable owing to different treatments of relaxation energies.

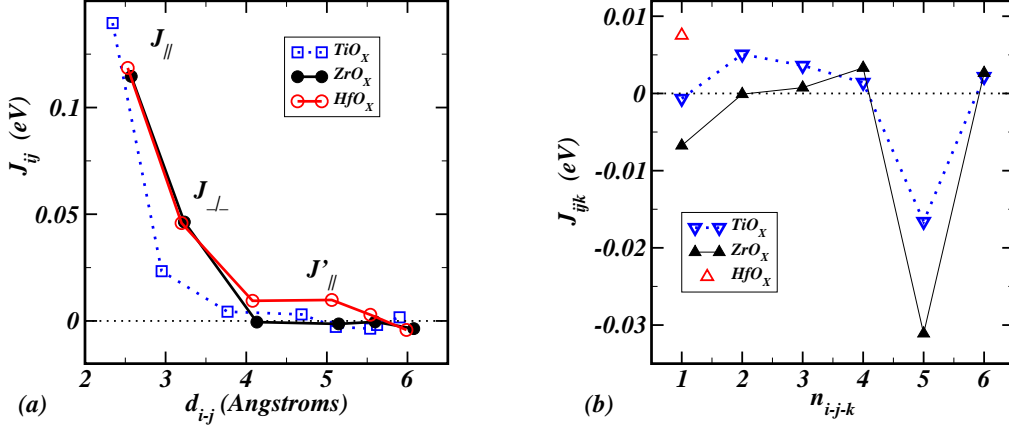


FIG. 2: Effective Cluster Interactions (ECI) for pair and 3-body interactions. Solid and dotted lines are to guide the eye. Results for the systems TiO_x (open blue symbols online), ZrO_x (solid black symbols) and HfO_x (open red symbols online). (a) The first two pair-ECI are for nearest-neighbor (nn) $O-[]$ pairs that are parallel- (J_{\parallel}) and perpendicular (J_{\perp}), respectively, to the hexagonal c-axis; the second pair parallel to c_{Hex} is J'_{\parallel} (pairwise-ECI are plotted as functions of inter-site separation), note that the results for HfO_x are very similar to those for ZrO_x except that the 3'rd and 4'th (J'_{\parallel}) nn-pairs are significantly larger in HfO_x ; (b) 3-body interactions are plotted as functions of the index n_{i-j-k} which increases, nonlinearly, as the area of triangle i-j-k increases. Large positive pairwise ECI imply strong pairwise $O-[]$ nn-attractions, i.e. strong pairwise $O-O$ nn-repulsions.

II. RESULTS AND DISCUSSION

A. Ground-States

The CE was used for a ground-state (GS) analysis that included all configurations of $[]$ and O in systems of 18 or fewer Hf -atoms (octahedral interstitial sites); a total of $2^{18} = 262,144$ structures (reduced by symmetry). Five GS were identified in the range,

$0 \leq X \leq 1/2$, i.e. at $X = 0, 1/6, 1/3, 5/12$ and $1/2$; solid circles (blue online) on the convex hull (solid line) in Fig. 1. The extension of the convex hull towards monoclinic hafnia (HfO_2) is also plotted in Fig. 1. The CE-results suggest that all four VASP-GS in the $\alpha Hf[1-X]O_X$ subsystem are also GS of the $Hf - O$ binary. The VASP-predicted maximum solubility of O in Hf is $X_{max} \approx 0.5$, significantly greater than the experimental value of $X_{max} \approx 0.28$.

Larger open squares (red online) in Figure 1 are CE-calculated values for the ΔE_f that correspond to the VASP calculations, and the smaller open squares (blue online) are ΔE_f for the remaining $262,144 - 106 = 262,038$ structures in the GS analysis. All space group determinations were performed with the FINDSYM program.^{25,31}

TABLE I: Crystal structure parameters for predicted ground-state phases in the $\alpha Hf[1-X]O_X$ system. Cell constants are given in Å.

System	X atomic fraction O	Space Group IT number Pearson Symbol	Calculated cell constants (Å)	Idealized Atomic Coordinates
Hf_6O	1/6 1/7	$R\bar{3}$ 148 hP7	$a \approx \sqrt{3}a_0$ $= 5.5391$ $c \approx 3c_0 = 15.183$	$O: 0, 0, 0$ $Hf: 1/3, 0, 5/12$ $Hf: 0, 1/3, 5/12$ $Hf: 2/3, 2/3, 5/12$ $Hf: 2/3, 0, 7/12$ $Hf: 0, 2/3, 7/12$ $Hf: 1/3, 1/3, 7/12$
Hf_3O	1/3 1/4	$P\bar{3}1c$ 163 hP16	$a \approx \sqrt{3}a_0$ $= 5.5391$ $c \approx 2c_0 = 10.122$	$O: 1/3, 2/3, 1/4$ $O: 2/3, 1/3, 3/4$ $O: 0, 0, 0$ $O: 0, 0, 1/2$ $Hf: 2/3, 2/3, 7/8$ $Hf: 1/3, 0, 7/8$ $Hf: 0, 1/3, 7/8$ $Hf: 0, 2/3, 5/8$ $Hf: 1/3, 1/3, 5/8$ $Hf: 2/3, 0, 5/8$ $Hf: 0, 1/3, 3/8$ $Hf: 2/3, 2/3, 3/8$ $Hf: 1/3, 0, 3/8$ $Hf: 1/3, 1/3, 1/8$ $Hf: 2/3, 0, 1/8$ $Hf: 0, 2/3, 1/8$

$Hf_{12}O_5$	5/12	$R\bar{3}$	$a \approx \sqrt{3}a_0$	$O: 0, 0, 1/12$
		148	$= 10.615$	$O: 0, 0, 11/12$
	5/17	hP17	$c \approx 6c_0 = 30.366$	$O: 0, 0, 1/3$
				$O: 0, 0, 2/3$
				$O: 0, 0, 1/2$
				$Hf: 2/3, 2/3, 13/24$
				$Hf: 1/3, 0, 13/24$
				$Hf: 0, 1/3, 13/24$
				$Hf: 1/3, 1/3, 11/24$
				$Hf: 2/3, 0, 11/24$
				$Hf: 0, 2/3, 11/24$
				$Hf: 2/3, 2/3, 3/8$
				$Hf: 1/3, 0, 3/8$
				$Hf: 0, 1/3, 3/8$
				$Hf: 1/3, 1/3, 5/8$
				$Hf: 2/3, 0, 5/8$
				$Hf: 0, 2/3, 5/8$
Hf_2O	1/2	$P\bar{3}1m$	$a \approx \sqrt{3}a_0$	$O: 0, 0, 0$
		162	$= 5.5391$	$O: 1/3, 2/3, 1/2$
	1/3	hP9	$c \approx c_0 = 5.0610$	$O: 2/3, 1/3, 1/2$
				$Hf: 1/3, 0, 1/4$
				$Hf: 0, 1/3, 1/4$
				$Hf: 2/3, 2/3, 1/4$
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				$Hf: 1/3, 1/3, 3/4$

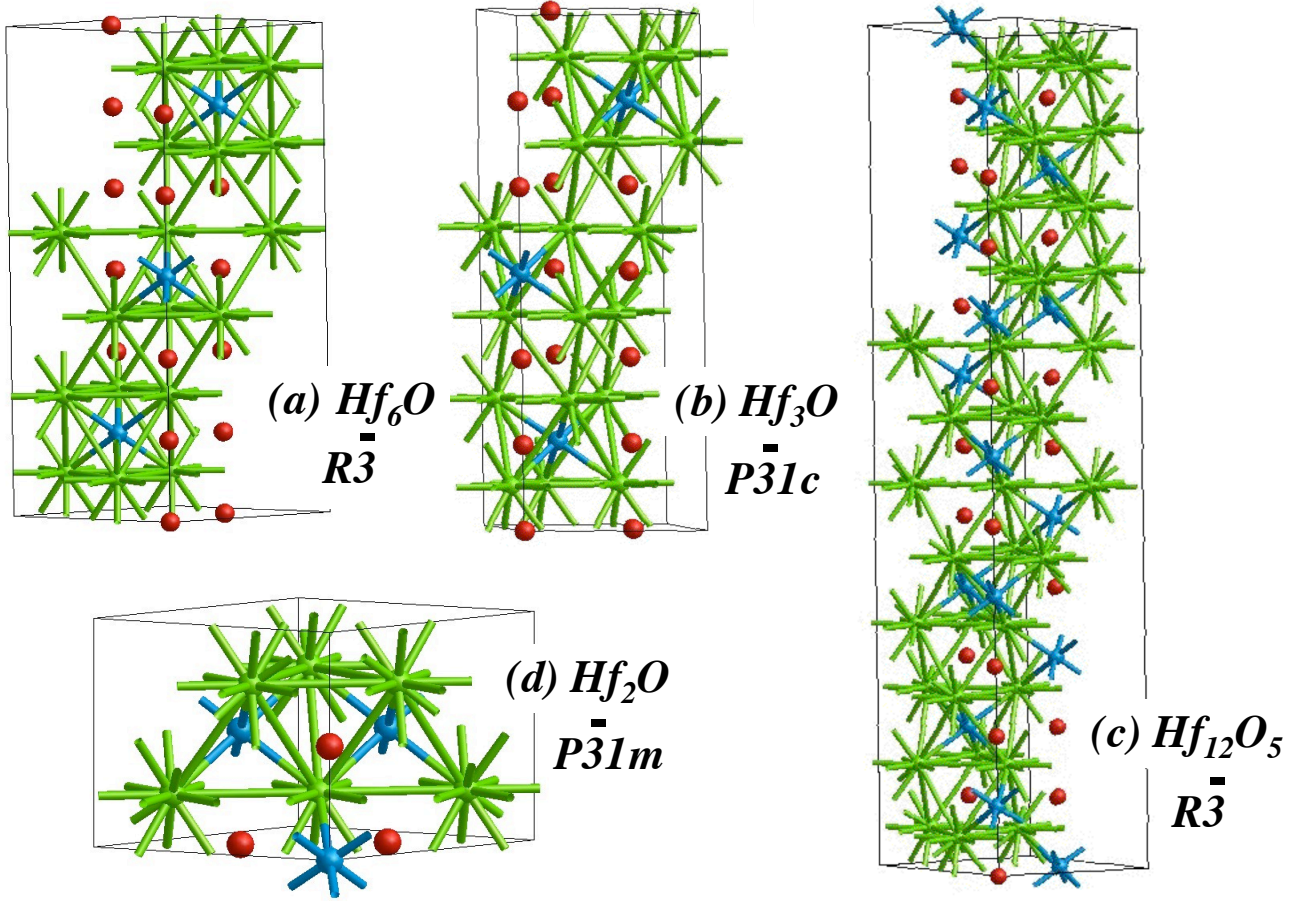


FIG. 3: Idealized crystal structures of the four cluster-expansion-predicted suboxide ground-states: (a) Hf_6O ; (b) Hf_3O ; (c) $Hf_{12}O_5$; (d) Hf_2O . Spheres connected by bond-sticks (yellowish-green online) represent Hf . Isolated spheres with bond-sticks (blue online) represent oxygen. Isolated spheres (red online) represent vacant octahedral sites.

Ground State crystal structures of the VASP- and CE-GS in $Hf-HfO$ are described in Table I and their idealized structures are drawn in Figures 3 a-d: where Hf is represented by spheres connected with bond-sticks (yellowish-green online); O is represented by isolated spheres with bond-sticks (blue online); and $[]$ are represented by isolated spheres (red online). As in the ZrO_x system, all GS structures are characterized by $O-O$ nn-avoidance both parallel- and perpendicular to c_{Hex} .

The VASP-CE-predicted $R\bar{3} Hf_6O$ GS is the same as the experimental low-T structure reported by Hirabayashi et al.¹⁸. Space group relations, require a first-order $P6_3mmc \rightleftharpoons R\bar{3}$ disorder \rightleftharpoons order transition between the $P6_3mmc$ disordered phase and the $R\bar{3} Hf_6O$ ordered phase. The Hf_6O GS is the only GS within the experimental solubility range $0 \leq X \lesssim 0.28$; all the other computationally predicted GS-phases are presumably metastable.

B. Finite Temperature Calculations

1. The Phase Diagram

A first principles phase diagram (FPPD) calculation was performed with conoical- and grand canonical Monte Carlo (MC) simulations using the emc2 code which is part of the ATAT package²⁷⁻²⁹. Input parameters for emc2 were: a simulation box with at least 4,050 octahedral sites; 2000 Monte Carlo passes. The predicted phase diagram is shown in Figure 4. Most phase boundaries were determined by following order-parameters (η) of the various ordered phases as functions of X and T. Dotted boundaries are used to acknowledge uncertainties in phase boundary determinations. In particular, boundaries of the possible Devil's Staircase (DS? in Fig. 4) regions are labeled DS?) are poorly defined, and the interior structures of these regions are undetermined.

2. Hf_6O

Interstitial ordering of O and $[]$ in hcp HfO_x was studied by Hirabayashi et al.¹⁸ who used electron- and neutron diffraction to analyse single crystals with bulk compositions in the range of $0 \leq at\% O \lesssim 20$ ($0 \leq X \lesssim 0.25$); described as $HfO_{1/6-}$ and $HfO_{1/6+}$ for samples with less than or more than one O -atom per six Hf -atoms. The structure that

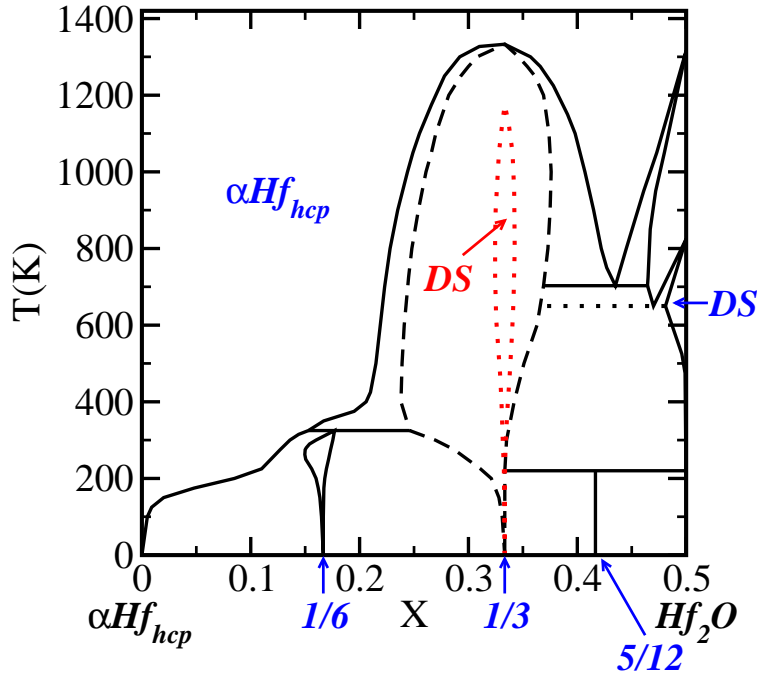


FIG. 4: Calculated phase diagram for the system $\alpha\text{Hf}[\]_{1-X}\text{O}_X$: Approximate regions in which the calculations predict a cascade of ordered phases is labeled DS to indicate possible Devil's Staircases of closely related ordered phases.

Hirabayashi et. al.¹⁸ report for $\text{HfO}_{1/6-}$ has $R\bar{3}$ space group symmetry and is identical to the VASP-GS at Hf_6O (Fig. 5 and Table I).

The FPPD-predicted order-disorder transition in Hf_6O ($\approx 325\text{K}$) is first-order (Fig.[?]), but significantly *lower* than than the experimental value ($\approx 700\text{K}$ ¹⁸) or the calculated value from Ruban et al. (600K ;³⁰ predicted transition-order not reported). Typically, FPPD cal-

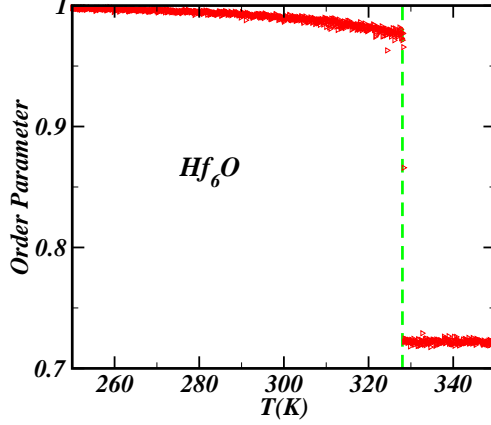


FIG. 5: Calculated order-parameter vs temperature (T) curve for the calculated 1st order transition in Hf_6O .

calculations *overestimate*] order-disorder transition temperatures so this result is surprising.

3. Possible Devil's Staircase in Hf_3O

The most O -rich structure determination in Hirabayashi et al.¹⁸ was for a sample with $X=0.203$. The reported structure has $P\bar{3}1c$ symmetry, and is equivalent to the predicted Hf_3O structure [Fig. 3(b), Table I] except that in the experimental sample, maximal O -site occupancy would be $\lesssim ([]_{0.16}, O_{0.84})$.

Figures 6a and b are plots of order-parameter vs. T for Hf_3O . The results plotted in Fig. 6a, were calculated with the MC-box-size held constant at 4,050 $O:[]$ -sites while the number of MC-passes is varried. Almost all the order-parameter plateaus are the same for different numbers of MC-passes, which reflects the influence of MC-box size on the ordered-phase periodicities that are allowed. Note that the transition temperatures from one plateau to another are clearly not converged. The results plotted in Fig. 6b were calculated with a constant numbers of MC-passes (12,000) and various MC-box-sizes; i.e. $O:[]$ -sites. Varying

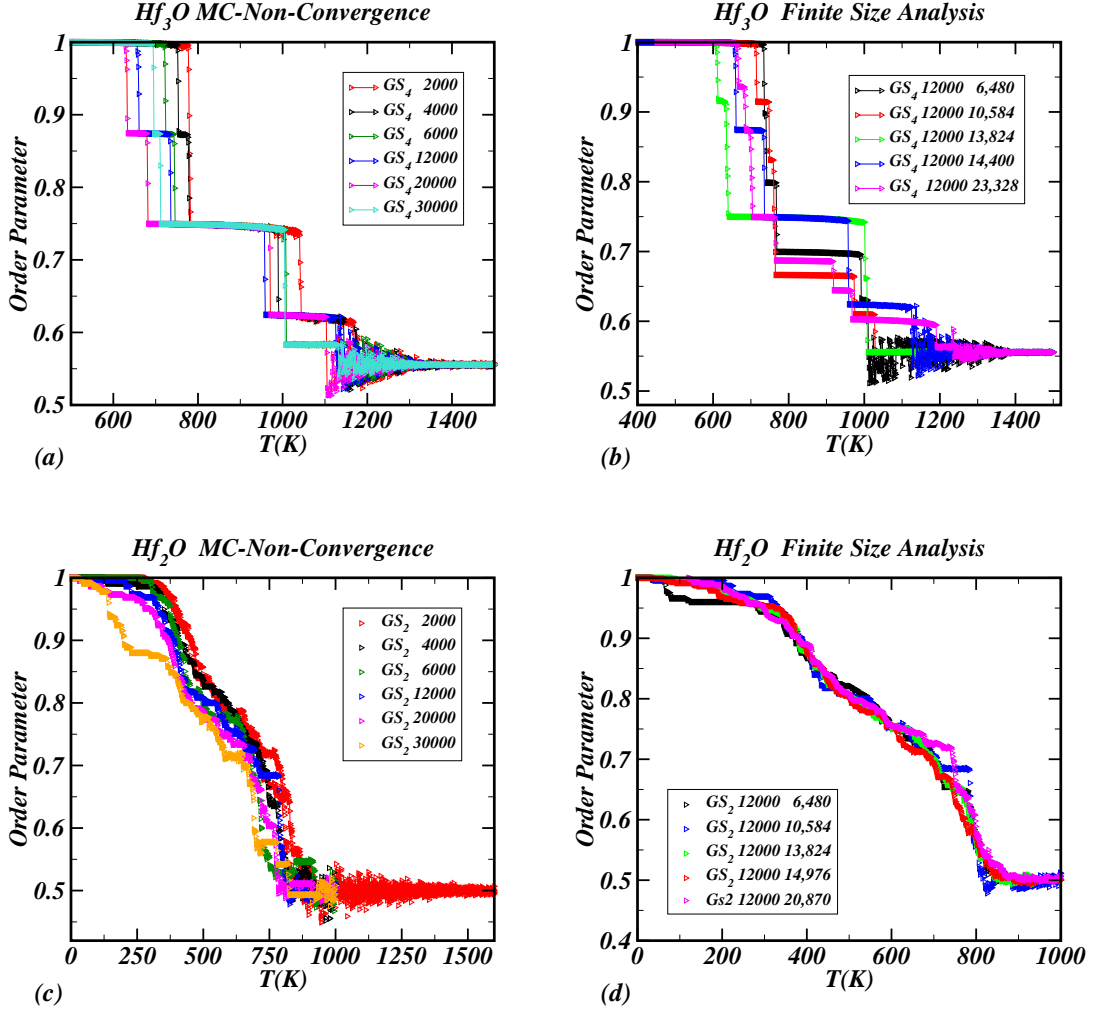


FIG. 6: Calculated order-parameter vs temperature (T) curves that evince possible Devil's Staircases (DS?) of closely related ordered phases at $X=1/3$ (a,b) and $X=1/2$ (c,d): (a,c) Monte-Carlo (MC) simulations at constant MC-box-size and different numbers of MC-passes at each T , almost always find the same set of ordered-phase plateaus (the notation GS_4 2000 means the simulation was started in the Hf_3O -GS and run for 2000 MC-passes per T); (b,d) Calculations at a constant number of MC-passes, with various MC-box-sizes yield different plateau sequences because box-size determines allowed periodicities for ordered phases (the notation GS_4 12,000 6,480 means the simulation was started in the Hf_3O -GS and run for 12,000 MC-passes per T , on an MC-box that contains 6,480 sites for $O:[\]$ mixing).

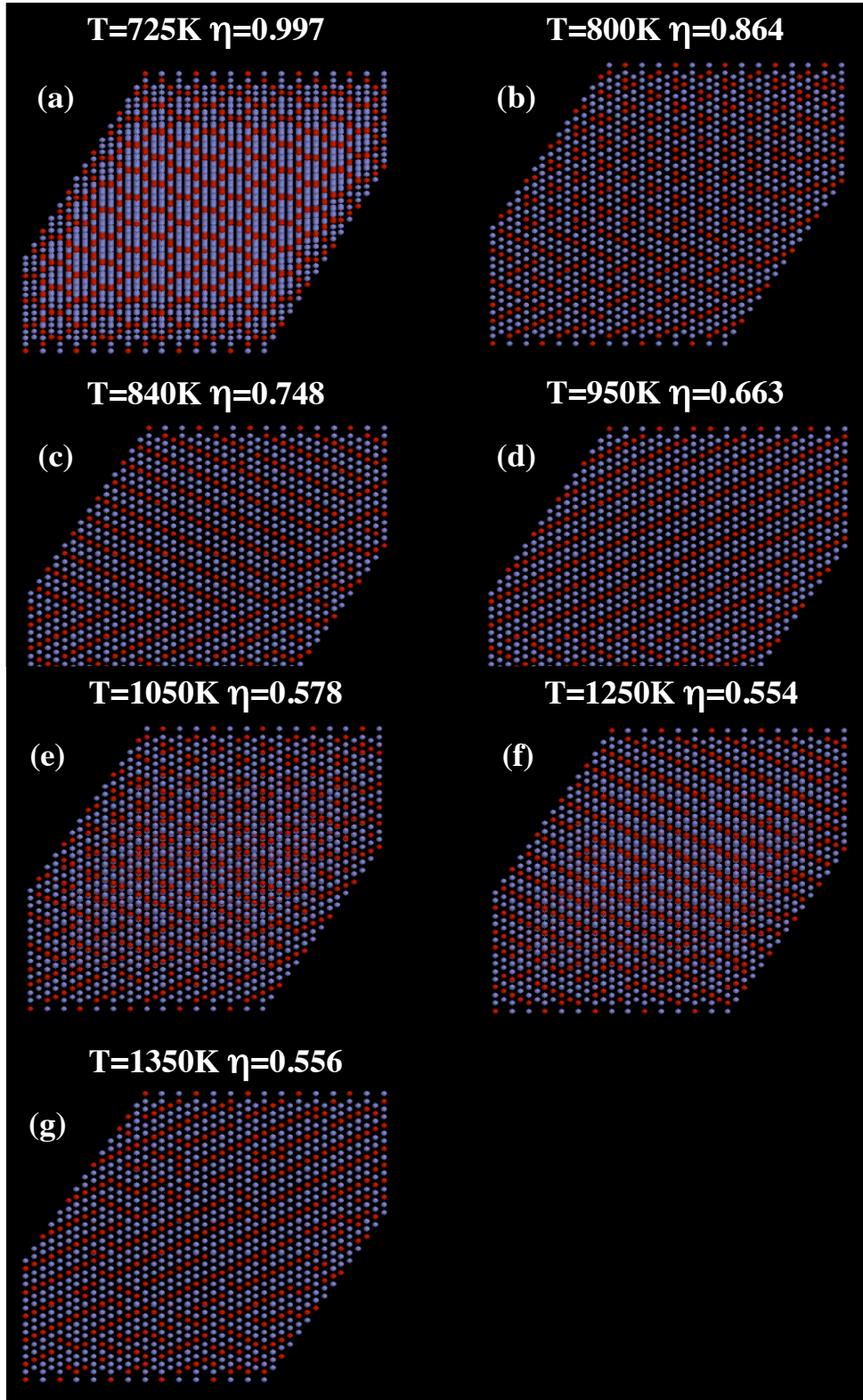


FIG. 7: MC snapshots of ordered phases in the possible Devil's Staircase in Hf_3O . For clarity, only O- (red online) and vacant-sites ([]-sites, blue online) are shown: (a) The GS-structure with minor disorder. In (b)-(g) there appears to be a competition between two ordering modes: 1) a striped mode (c,d,f,g) in which layers \perp to c_{Hex} have single O-rows that alternate with i double-[]-rows; 2) a triangular mode (b,e) in which layers \perp to c_{Hex} exhibit an ordered array of O_3 -nn-equalateral triangles and []₆-nn-equalateral triangles.

MC-box-size allows different ordered-phase periodicities; i.e. allows access to more stairs in the cascade of ordered phases.

In Fig. 7a-g Monte Carlo snapshots are shown at seven different temperatures. For clarity, only O- (red online) and []-sites (blue online) are shown. These MC-snapshots appear to indicate a competition between two ordering modes: 1) a striped mode (c,d,f,g) in which layers \perp to c_{Hex} exhibit single O-rows that alternate with double-[]-rows; 2) a triangular mode (b,e) in which layers \perp to c_{Hex} exhibit ordered arrays of O_3 -nn-equalateral triangles and []₆-nn-equalateral triangles. It is not clear if this cascade of ordered structures constitutes a Devil's Staircase, but the results presented in Fig. 6a and b suggest that it does.

4. Possible Devil's Staircase in Hf_2O

In Figures 6c and d, one sees similar order-parameter vs. T systematics for Hf_2O as one finds in Figures 6a and b for Hf_3O ; except that the density of plateaus is much greater in Hf_2O , because a 1:1 O:[]-ratio allows a greater number different periodic ordered structures than a 2:1 O:[]-ratio.

III. CONCLUSIONS

Ground-State ordered phases are predicted at $X=0$, $1/6$, $1/3$, $5/12$ and $1/2$, but only those at $X=0$ or $X=1/6$ are likely to be physically realized because the experimental value for the maximum solubility of O in hcp HfO_X is $X_{max} \approx 0.28$.

Observed ordered phases at $X=1/6$ and $X=0.203^{18}$ agree with predicted GS at $X=1/6$ and $X=1/3$ (but with diluted O -site occupancies).

In the metastable portion of the HfO_X phase diagram, $(0.28 \gtrsim X)$ cascades of ordered phases, possible Devil's Staircases, are predicted for bulk compositions near Hf_3O and Hf_2O .

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- ²⁵ Disclaimer: the use of a specific software package should not be misinterpreted as implying a

NIST endorsement of that package.

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